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TEMPLATE BASED NANOMANUFACTURING

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TEMPLATE BASED NANOMANUFACTURING

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ABSTRACT

Have you ever wondered how a gecko can walk up a glass window? Many species of gecko have unique features on their toes, a unique foot-hair structure that could wide scope of applications if successfully mimicked. This MQP takes several steps toward manufacturing Y-junction carbon nanotubes through a chemical vapor deposition growth process to be used as a building block for mimicking gecko foot-hairs.

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1. Introduction

1.1 Purpose

The gecko is a lizard having many unique attributes, including its well-known ability to walls, cling to vertical rock faces or trees (Bartlett and Bartlett, 14). These great climbers are able to traverse otherwise difficult surfaces due to specialized toe pads. The structure of a gecko's toe pads consists of layers of proportionally smaller hairs, the smallest layer measurable on the nanometer scale. Inspired by the unique attributes of the gecko foot-hair (setae) and the importance of the ability to mechanically adhere to smooth surfaces, this MQP seeks to explore the use of carbon nanotubes (CNT) as the basic building block to mimic the structure of a gecko's setae through the development of a manufacturing system to grow CNT and the subsequent use of that system to create a Y-junction CNT growth template.

1.2 Goals

We hope to provide a foundation for future groups of students to begin researching the mechanical properties of Y junction carbon nanotubes. In order to accomplish this, this project will consist of research into the history and importance of both straight walled and Y-junction carbon nanotubes. We will research and utilize a Chemical Vapor Deposition (CVD) system to grow carbon nanotubes in the Washburn Laboratory Facility at WPI. We also hope to specify explicit procedures for preparing thin aluminum samples as alumina nanopore growth templates for growing Y junction carbon nanotubes. Accomplishing these goals will provide a foundation for future MQP

teams to further develop strategies for creating a structure similar to the gecko setae system.

1.3 Report Layout

This report is comprised of five chapters. The first chapter is a brief introduction to our project. The second chapter provides an in-depth background into the technologies used in our project, including a history and importance of straight walled carbon nanotubes, Y junction carbon nanotubes, and the use of CVD systems to manufacture CNTs. The third chapter describes in detail the procedures and methodology we have used to manufacture Y junction nanotubes as well as methods for material characterizations. The fourth chapter focuses on project results. In the fifth chapter, we have drawn our conclusions and discuss potential future results building on the accomplishments of this project. References we have used to aid us through the entire project are included at the end of the main text. The appendices of this report contain additional images from our samples, a process flow chart, the detailed laboratory procedures we have used, as well as other relevant data.

2. Background

2.1 Gecko Foot Hair Structure

The amazing climbing ability of geckos has attracted the interest of philosophers and scientists alike for centuries. Only in the past several years has progress been made in understanding the mechanism behind this ability, which relies on sub-micrometer keratin hairs (setae) covering the toes of geckos feet. Each setae (which are roughly 5 microns in

diameter and are very elastic) is split into nanometer sized structures called spatulas. Spatulae are on average are 200 nanometers in diameter (1/250th of a human hair) and there are 14,000 of these tiny hairs per square millimeter! When in contact with a surface, each spatula produces a miniscule force of approximately 10^{-7} N (due to Van der Waals forces) (Sun, 1). Millions of spatulas acting together create enough adhesive force to keep geckos firmly attached to a surface, even when upside down on a glass ceiling.

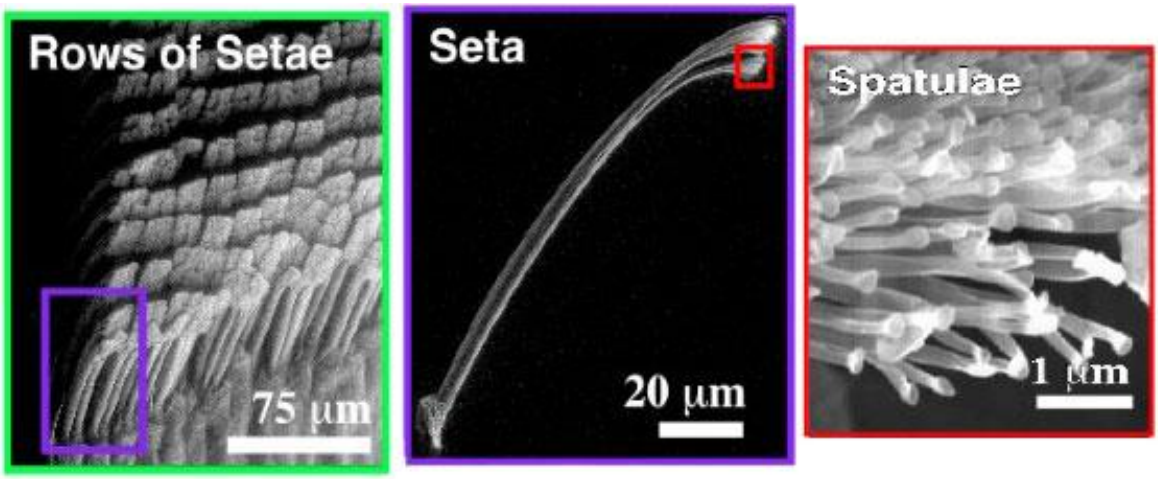

Figure 2-1: Decreasing Magnitudes of Size in Gecko Foot Hair

(Gaurav Shah and Metin Sitti)

When geckos run, their feet attach and detach 15 times per second. In order to stick and unstick their feet so quickly, gecko toes curl backward. When geckos attach to surfaces, their toes uncurl in a process that resembles inflation of a party favor. This process places the spatula-shaped tips in contact with the surface. To detach, geckos peel their toes away from a surface the way tape is removed, lifting first from one end because this action detaches the hairs one at a time.

Geckos can stick to metal, plastics or glass, suspended in the air or under water. Engineers predicted the force of a single gecko foot hair by measuring the adhesive force

of a whole gecko and dividing that by the number of foot hairs per animal. It turns out a gecko foot exerts a force of 10 Newtons (about 2.2 Pounds). A million hairs could fit onto a dime-sized area capable of supporting about 20 kilograms (about 44 pounds) of gecko (Geim, 462).

2.2 Van der Waals Forces

The unique structure of individual setae significantly increases the contact area between the gecko's toes and the surface upon which it walks. Greater surface area contact means closer interaction between the molecules of the setae and contact surface (the distance between the molecules of each material becomes very small). As the distance between the molecules of each surface decreases, typically 1 to 10 nm (Kendall, 1), weak intermolecular forces between the atoms and molecules of the setae and contact surface – called Van der Waals forces – are greatly magnified. The Van der Waals forces are normally so small they are insignificant to a vast majority of mechanical engineering calculations. In the setae system these forces are magnified so much that they are the mechanism causing the gecko to be able to stick to or climb up almost anything!

Van der Waals forces are the intermolecular forces responsible for many properties of matter, including melting points, boiling points, surface tension, densities and crystal structures (e. g. the shapes of snowflakes, sugar cubes, etc). Van der Waals' force is a general term that includes all intermolecular forces that act between electrically neutral molecules (or between parts of the same molecule) other than those due to covalent bonds, hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules or charged molecules. These electrostatic forces are divided into three main categories:

- Permanent dipoles (or polar molecules): These forces (Keesom forces) are present between two atoms in a molecule that have substantially different electronegativity: One atom attracts electrons more than another, becoming more negative, while the other atom becomes more positive. Water (H_20) is an example of a polar molecule.
- Instantaneous dipoles (Debye force): These forces are present due to chance when electrons happen to be more concentrated in one place than another in a molecule, creating temporary polarity in a molecule.
- Induced dipoles (London dispersion force): These forces occur when one molecule with a permanent dipole repels another molecule's electrons, inducing a dipole moment in that molecule. A molecule is polarized when it carries an induced dipole.

All materials experience an attraction to other materials due to London dispersion forces. As previously stated, in most situations these electrostatic attractions are so small and random they can be ignored. In the setae system, the sum of the dispersion forces over the area of their feet give geckos their adhesive toes.

When calculating the adhesive force of each toe, we look to equations that define the link between the adhesion mechanism (London dispersion forces) and unit area. A classical approach to defining the force equations for the mechanical force of adhesion in particular geometries is to calculate the pressure force of adhesion per unit area of contact:

$$Fadhesive = \frac{P}{area}$$

Equation 1 where $F_{adhesive}$ = force in Newtons, area = contact area in square meters, and P = pressure in newtons per square meter (N/m^2).

The following equation generalizes London dispersion forces, and was predicted in the 1930s by De Boer and Hamaker:

$$Fadhesive = \frac{P}{Area} = -\frac{A}{24\pi z^3}$$

Equation 2 where P is the force (negative for attraction), z is the distance between molecular nuclei, and A is a material-specific constant called the Hamaker constant (Kendall, 1).

Using a theoretical Hamaker constant value between gold and a single walled CNT (Nakajima, Yang, Fukuda, and Arai, 251), we can plot the relationship between the adhesive force and the distance between the molecules (z).

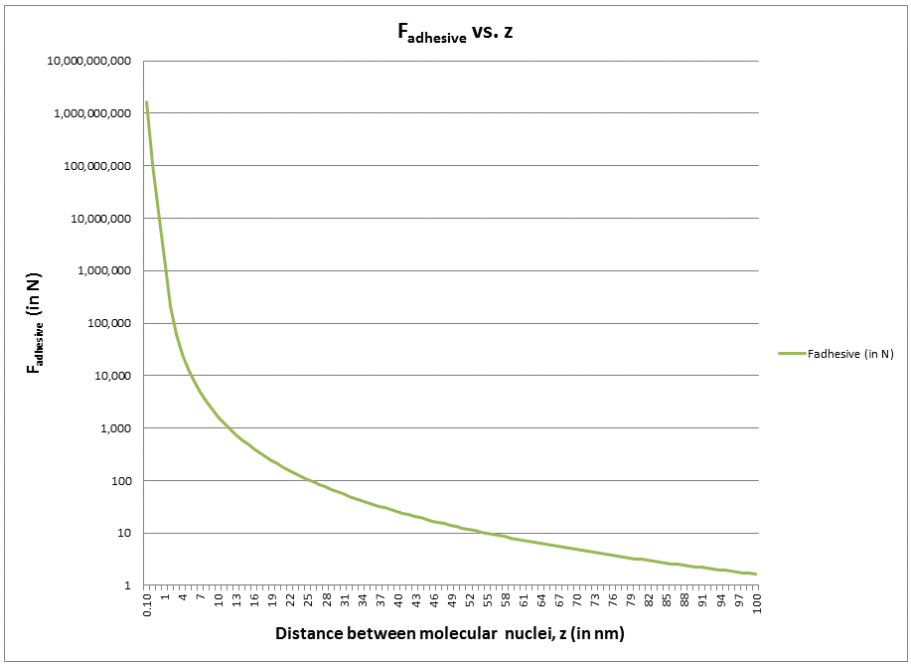

Figure 2-2-2 $F_{adhesive}$ vs Distance between molecular nuclei, 0-100nm

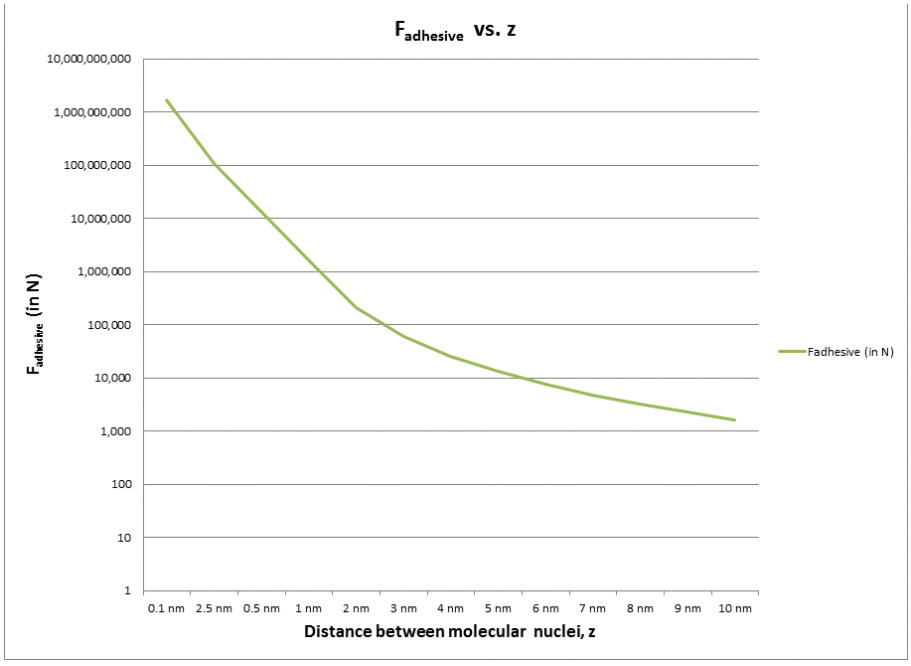

Figure 2-2-3 $F_{adhesive}$ vs Distance between molecular nuclei, 0.1-10nm

One can generalize from this analysis that as the distance z decreases $F_{adhesive}$ increases exponentially for distances less than 10 nm. Other studies (Autumn, 1081) have shown that a tokay gecko of approximately 50 g in weight (setae N) could theoretically generate 1,300N (133 kg force). This suggests that only 0.04% of its setae need to attach to support its weight on a vertical surface. This data implies that biomimicry of the setae system would have to be marginally successful in order to duplicate the adhesive properties of the setae system. A structure comprised of carbon nanotubes similar to the structure of the setae on a gecko's toes would likely have a similar adhesive nature.

2.3 Carbon Nanotubes

Carbon nanotubes are long, thin cylindrical molecules of carbon with properties that make them potentially useful in a wide variety of applications (e.g., nano-electronics, optics, materials applications, etc.). Discovered in 1991 by S. Iijima, (Iijima, 56) these macromolecules are unique for their size, shape, and remarkable physical properties. They exhibit extraordinary strength and electrical properties, and are efficient thermal conductors.

They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These structures have sparked the interest of many researchers in recent years, and a tremendous amount of research has been dedicated to the understanding of their physical properties. The difficulty in studying nanotubes is that they have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist).

2.3.1 History of the Nanotube

1985	Fullerenes discovered
1991	January – Nanotubes discovered at NEC, by Japanese researcher Sumio Iijima.
2001	April - IBM announces a technique for automatically developing pure semiconductor surfaces from nanotubes.
2002	REBO method of quickly and accurately modeling classical nanotube behavior is described.
2003	April - Demonstration proves that bending changes resistance.
	June - High purity (20% impure) nanotubes with metallic properties were reported to be extracted with electrophoretic techniques.
	September - NEC announced stable fabrication technology of carbon nanotube transistors.
2004	June - Scientists from China's Tsinghua University and Louisiana State University demonstrated the use of nanotubes in incandescent lamps, replacing a tungsten filament in a light bulb with a carbon nanotube one.
	March - Nature published a photo of an individual 4 cm long single-wall nanotube (SWNT).
	August - Varying the applied voltage emits light at different points along a tube.
2005	August - Nanotube sheet synthesized with dimensions 5 x 100 cm.
	September - Applied Nanotech (Texas), in conjunction with six Japanese electronics firms, have created a prototype of a 25-inch TV using carbon nanotubes. The prototype TV does not suffer from "ghosting," as some types of digital TVs do.
	September - Korean scientists lead by Pohang University of Science and Technology Professor Kim Kwang-Soo succeeded in pulling out a nested tube from a multiwalled nanotube (MWNT), extracted 1 millimeter.
	November - Liquid flows 5 times faster than predicted through array
2006	January - Thin films of nanotubes made by evaporation
	January - Elasticity increased from 20% to 280% by raising temperatures, causing diameter and conductivity to change greatly
	March - IBM announces that they have built an electronic circuit around a CNT.
2009	April - Nanotubes incorporated in virus batter
	A single-walled carbon nanotube was grown by chemical vapor deposition across a 10-micron gap in a silicon chip, then used in cold atom experiments, creating a blackhole like effect on single atoms. Anne Goodsell, Trygve Ristroph, J. A. Golovchenko, and Lene Vestergaard Hau
2012	January — IBM creates 9nm carbon nanotube transistor that outperforms silicon
2013	September - Researchers build a Carbon nanotube computer.
Source: *Wikipedia*	

Figure 2-4: A Schematic of Single Wall Carbon Nanotube

(http://www.ewels.info/img/science/nanotubes/tube.angled.jpg)

2.3.2 CNT Categorization

There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). They are composed entirely of carbon atoms bonded by sigma (σ) bonds, specifically sp^2 hybridized bonds similar to those of graphite. This bonding structure, stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces. Under high pressure, they can merge together, trading some sp^2 bonds for sp^3 bonds, giving great possibility for producing strong, unlimited-length wires through high-pressure nanotube linking.

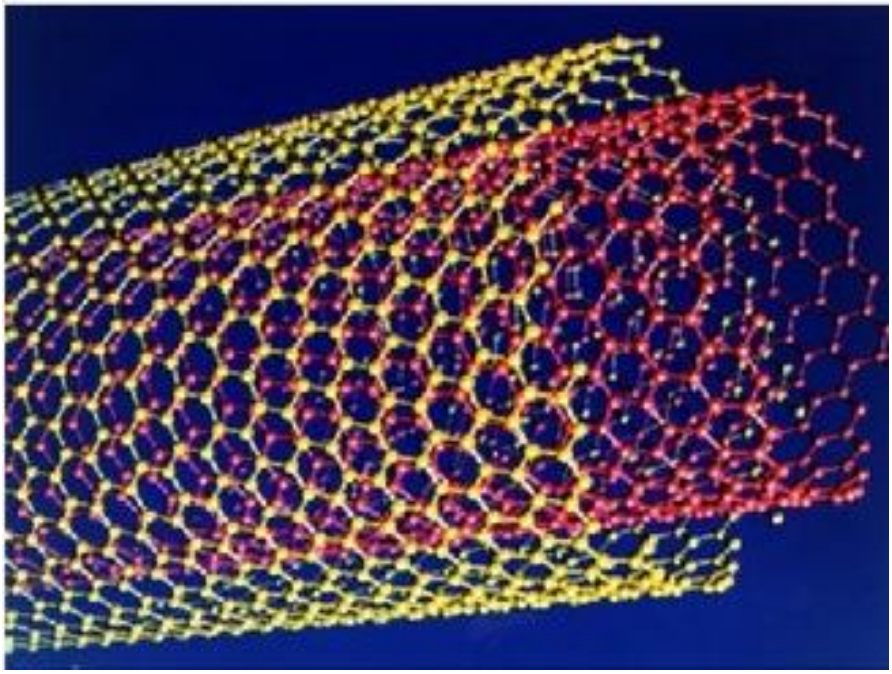

Figure 2-5: Multiwall Carbon Nanotube (www.nec.com)

Carbon nanotubes can be made in a variety of types. They can be single walled or have multiple walls (example above in Figure 2-5). Nanotubes can be described by the chiral vector (n, m), where n and m are integers of the vector equation R = na1 + ma2.

The values of n and m determine the chirality, or twist, of the nanotube. The chirality in turn affects the conductance, density, lattice structure, and other properties. A SWNT is considered metallic if the value n - m is divisible by three. Otherwise, the nanotube is semi conducting. Given the chiral vector (n,m), the diameter of a carbon nanotube can be determined using the relationship:

$$d = (n2 + m2 + nm)^{1/2}\ 0.0783 \text{ nm}$$

Equation 2-3: Diameter of Carbon Nanotube

CNT are further categorized by this vector equation in the following manner: If R lies along the armchair line (thin yellow line, R=0°), the SWNT is called an "Armchair" nanotube. If R=30° the tube is called a "zigzag" nanotube, otherwise R >30° is known as

a “chiral” nanotube. The vector a1 lies along the "zigzag" line. The other vector a2 has a different magnitude than a1, but its direction is a reflection of a1 over the Armchair line. When added together, they equal the chiral vector R.

2.3.3 Properties of Carbon Nanotubes

CNT’s are one of the strongest materials known to man in terms of tensile strength and elastic modulus. In 2000, an MWNT was tested to have a tensile strength of 63 GPa (Srivastava and Wei, 220). In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. CNTs also have very high elastic modulus, in the order of 1 TPa (Qian et al, 435). Since carbon nanotubes have relatively low density, the strength to weight ratio is exceptional. Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. CNTs are not nearly as strong under compression. Due to their hollow structure, they tend to undergo buckling when placed under compressive, torsional or bending stress. Yardumakan et al, have shown that carbon nano tubes do appear to conform to the surfaces around them and provide a great surface to resist motion perpendicular to the longitudinal axis of the tubes. Northen and Turner have shown that a dissimilar structure involving nano hairs arranged in a grid pattern, affixed to the top of a micro fiber sized “column” increased the ability of their samples to conform to the irregularities in a surface, and the ability of the samples to resist perpendicular forces. These material characteristics make CNT’s an ideal candidate for mimicking the setae system.

2.2.4 Synthesis of carbon nanotubes

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD). Of these, the CVD method has shown the most promise in terms of price per unit cost (most cost efficient). The CVD process generally involves a reaction of carbon-containing gas (such as acetylene, ethylene, and ethanol) with a metal catalyst particle (such as cobalt, nickel, or iron) at temperatures above 600°C.

Carbon nanotubes are not necessarily products of high-tech laboratories; they are commonly formed in "ordinary" places such as candle flames. However, these naturally occurring varieties (due to the highly uncontrolled environment in which they're produced) are highly irregular in size and quality – they lack the high degree of uniformity necessary to meet the needs of both research and industry.

Y-junction carbon nanotubes are CNT with a unique shape and properties. By modifying the CVD growth process, it is possible to produce these specialized CNT. The CVD growth process is based upon growing CNT in an alumina template, which ultimately determines the shape of the grown tubes. Modifications to the anodization process used to produce the template forces the nanochannels that form in the alumina to split in the shape of a Y.

2.4 Chemical Vapor Deposition

Chemical vapor deposition is widely used in the semiconductor industry during fabrication of semiconductor devices. It is typically used to deposit very thin films of materials such as silicon oxide or silicon nitride onto a semiconductor surface (Pierson, 26). This MQP uses template assisted chemical vapor deposition (CVD) to grow carbon

nanotubes. During the procedure developed herein, the CVD system deposits carbon in the nanochannels of our alumina template, which results in the growth of the carbon nanotubes in the shape of those channels. For practical purposes to maintain the focus of this project, a detail discussion of the theories and chemistry behind chemical vapor deposition are not discussed here. Instead a general background of CVD systems, how carbon nanotubes are grown in CVD systems, and the design of our CVD system are described.

2.4.1 What is Chemical Vapor Deposition

Chemical vapor deposition is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit (Pierson, 36). The theory behind CVD is complex, and involves aspects from disciplines such as chemistry, fluid dynamics, thermodynamics and kinetics. In this report, we will give a very basic background on CVD systems and how they work. (It is recommended that you read the *Handbook of Chemical Vapor Deposition,* which is an in-depth primer on chemical vapor deposition, the theories and mathematics behind CVD).

There are a large number of different methods of CVD, including low pressure, ultra high vacuum, atmospheric pressure, rapid thermal, and plasma-enhanced (LPCVD, UHVCVD, APCVD, RTCVD and PECVD respectively). Each of these different methods have their own benefits and ideal applications. The basic principle of chemical vapor deposition is that a thin film or surface of a chemical compound is deposited on the surface of a certain substrate. The deposited material has some chemical composition that is normally capable of being created using some form of thermal decomposition or oxidation process.

There are five basic steps to every CVD process: vaporization of precursor molecules into the furnace or reactor, diffusion of the precursor molecules onto the surface of the substrate, absorption of the precursor molecules onto the surface of the substrate, decomposition of the precursor molecules and their incorporation into the substrate surface, and finally recombination of the byproducts of the reaction and their subsequent removal from the reaction chamber.

2.4.2 Growth of CNT in CVD

During the thermal decomposition of the acetylene gas (C_2H_2), carbon atoms are broken free from the hydrogen atoms, which allows the carbon atoms to be deposited on the surface of a substrate within the reaction chamber, while the hydrogen atoms form a byproduct of hydrogen gas.

$$C_2H_2 + \text{energy} \rightarrow 2C + H_2$$

Equation 2-4: Pyrolisys of Acetylene

This is the driving reaction behind the growth of carbon nanotubes in a CVD system. While acetylene is not always the gas used as a precursor in the reaction, it is the primary gas used in our particular CVD system.

While it is possible to control the thickness of a deposited layer, it is usually difficult to control the actual location of deposition. As such, a catalyst can be used to increase the likeliness that carbon will be deposited at a desired location. In our reaction, a cobalt catalyst is deposited at the bottom of the nanochannels in the alumina substrate. These cobalt nanoparticles act as catalysts to help to control the deposition of the carbon in the nanochannels.

The deposition continues until an amorphous layer of carbon forms on the very top surface of the alumina substrate. This thin layer of amorphous carbon should be removed prior to attempting any testing of the carbon nanotubes within the substrate, or before attempting to remove the nanotubes from the substrate.

2.4.3 Design of CVD System

The basic design of our CVD system was dictated by the number of gases we use, the size of our furnace, and the limitations of our lab space. During the process of preparing for this project, we researched the general theory and design of CVD systems, and felt that the typical approach of a vacuum system and exhaust on one side of the furnace process tube, and the precursor gases on the opposing side of the process tube to be the ideal design for our layout. In our lab setup, the precursor gases are placed on the right hand side of the process tube, while the vacuum pump and exhaust for the system are placed on the left hand side.

During the general installation process it was necessary to determine the exact placement and layout of our system, as well as create a schematic that could be used for the construction process and as a record of the layout. Decisions we had to make included how to plumb the various gases to the process tube, whether to use a dividing manifold, or a single flow system, how to control each of the gases, as well as how to best take advantage of the limited space we had for the CVD system.

In the end, it was decided to use a single flow system, in which all of the precursor gases are controlled by a valve placed in the system after the gas regulator. All lines leading from gas canisters go to a system shutoff valve, which serves as a way to shut off all possible gas flow through the system. A flow meter is next in the system,

which allows us to monitor the flow of gas through the system, and aids us in determining if the system has been purged of any gas prior to beginning our procedure. After the flow meter, but before the furnace process tube is a pressure gauge, which allows us to determine if the system is under vacuum, as well as serves as a way to ensure that the gases are being delivered properly to the system.

The furnace and process tube are the next major component in the system. A Thermolyne 79300 tube furnace was chosen for its ability adapt to furnace tubes ranging in 1 inch to 3 inches in size, as well as it's ability to accurately heat to 100-1200°C, and is a single zone, split tube furnace, and features a 12 inch heating zone. We use a 25mm outer diameter, 22mm inner diameter Quartz process tube.

On the left hand side of the furnace process tube is a pair of three-way valves. The first of which serves the vacuum pump, which allows us to open the vacuum pump to the atmosphere, shut off flow to the vacuum pump, or direct the flow from the process tube to the vacuum pump. The second of which allows us to direct the flow from the process tube to the vacuum pump, stop flow from the process tube, or direct flow to the exhaust hood in our lab.

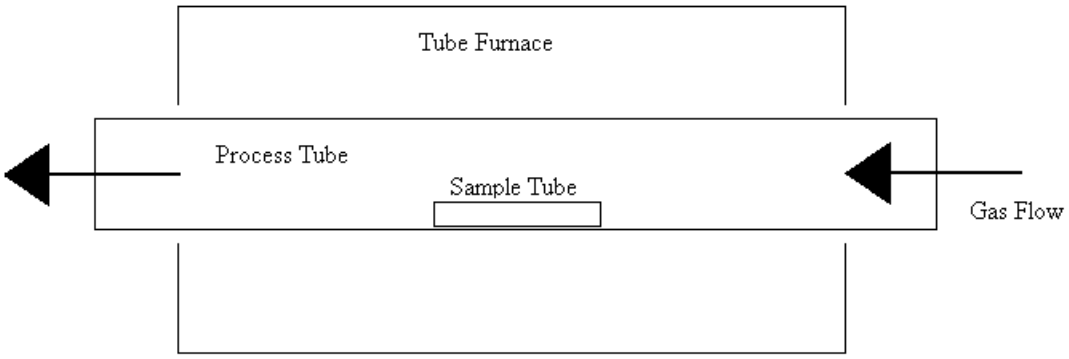

Figure 2-6: Basic Schematic of a CVD system

(Note: This project originally planned to utilized nano-indentation and atomic force micrscopy to begin to characterize mechanical properties of Y-Junction CNT's. However, due to schedule constraints (training, general system installation delays, and process learning), the use of these technologies was not included in this research project. However, as a significant effort regarding the use of these technologies was investigated, they are briefly discussed in the next two sections of the report.

2.5 Nano-indentation

Nanoindentation is a method for determining the hardness of a material very similar to conventional indentation or microindentation tests such as the Rockwell or Vickers hardness tests, each of which results is used for a different scale, Knoop being used for the microscale respectively. During a conventional indentation hardness test, an

object of a known geometry is placed on the surface of the material being tested. A force is then applied to this indenter, and depending on the type of indentation being done, a formula is used to calculate the hardness of the material being tested based upon certain criteria. For instance, the Vickers hardness of a material (H_v), is the result of the force being applied to the indenter divided by the area of the impression left by the indenter (Equation 2-3).

$$H_v = \text{Load (kgf)} / \text{ Impression area (mm}^2\text{)}$$

Equation 2-5

While similar in methods and concepts to conventional indentation testing for hardness, nanoindentation uses an indenter whose physical geometry is measured on the nanometer scale, and whose impressions are also on the nanometer scale. This means regular methods of measuring the indentations, such as optical microscopy or using a physical measuring device, cannot be used. While it is possible to use Scanning Electron Microscopy to determine the areas of the indentations left in a material, it is not practical to use, as it is very time consuming to find and image such small indents. Instead, methods have been devised that allow for continuous measurement of the loading applied, as well as the displacement of the indenter and time. The advantage of using nanoindentation is that it allows for the measurement of the elastic and plastic material properties of the sample (Bhushan, 504).

2.6 Atomic Force Microscopy

The fundamental difference between Atomic Force Microscopy (AFM) and nanoindentation is that during a nanoindentation experiment an external load is applied to the indenter tip (Bhushan, 499). Atomic force microscopy, similar to other scanning probe microscopes uses piezoelectric stacks to move a probe in the lateral and vertical planes. To use an AFM to measure mechanical properties, a hard tipped probe is mounted on a cantilever beam, which is then brought extremely close to the sample material. The elastic deflection of the cantilevered beam as a result of any attractive or repulsive forces acting on the probe tip is recorded, and this deflection can then be used to determine the forces acting on the tip of the probe. When the tip of the probe comes into contact with the surface, it experiences both the attractive intermolecular forces as well as an elastic repulsive force as a result of the physical properties of the material. In the case of the gecko foot hair structure, the attractive intermolecular forces are far larger than the repulsive elastic forces from surface contact, and as such, there is a net attractive force on the gecko's foot. This allows a gecko to adhere to any surface it touches, even if that surface is wet.

2.7 Scanning Electron Microscopy

The scanning electron microscope (SEM) is a type of microscope capable of producing high resolution images of a sample surface by directing an electron beam onto a sample and measure the deflections of the electrons. A byproduct of using this measurement technique is that SEM images have a three-dimensional appearance and can

be used for examining the surface structure of samples. A Field Emitting Scanning Electron Microscope (FESEM) was employed in this project in order to image samples.

In an FESEM, electrons generated by a field emission source are accelerated in a magnetic field gradient. The beam passes through an electro-magnetic lens, which focuses the beam onto the sample. As result of this bombardment, different types of electrons are emitted from the beam generator. A detector measures the deflections of the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the primary scanning electron beam. Finally, the image is displayed on a monitor.

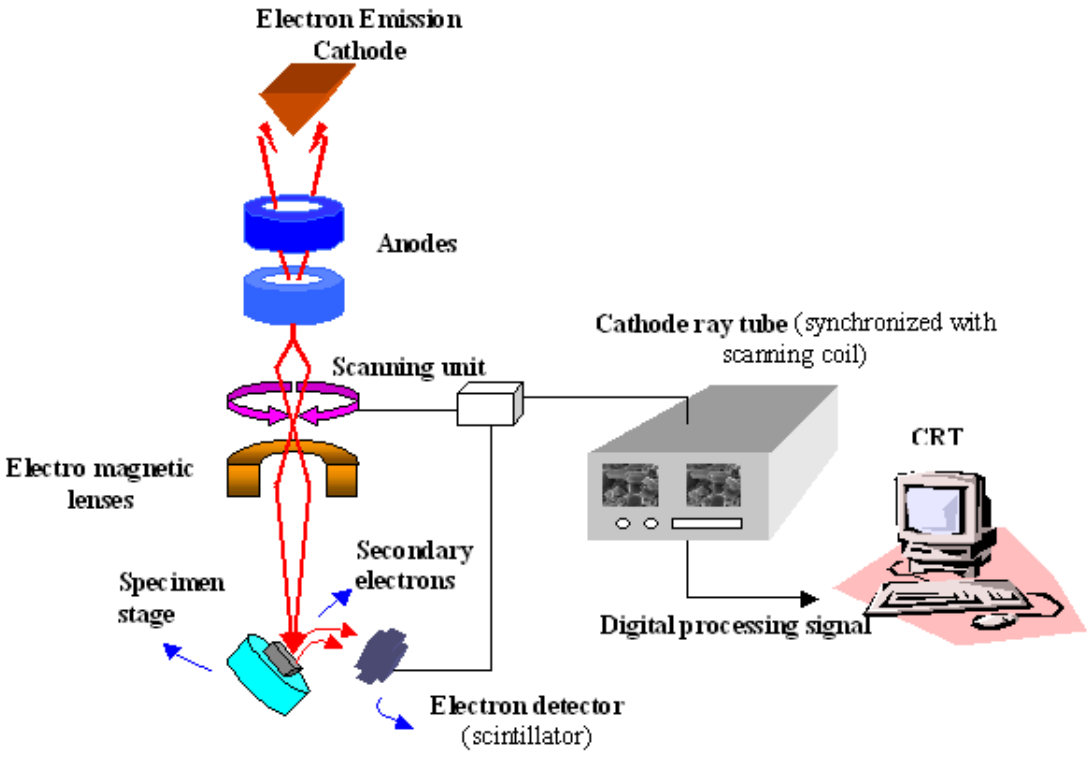

Figure 2-7: FESEM Principle of Operation

(http://infohost.nmt.edu/~maximino/FESEM%20principle.gif)

FESEM's are capable of producing images of 800,000X magnification. This project utilized a LEO 986A FESEM to image samples. Since WPI does not have this high resolution machinery, an agreement was reached between Harvard's Center for Nanoscale Systems to use this type of equipment.

3. Methodology

While the measurement of the mechanical properties of individual and groups of carbon nanotubes is possible, we are more interested in the collective properties of carbon nanotubes, especially Y junction nanotubes grown by template assisted growth technique. Our method starts at the anodization of an annealed high purity aluminum strip. During anodization a Y shape nanopore array forms in the alumina template. Those Y shape nanochannels form the foundation for our carbon nanotubes. A cobalt catalyst is then deposited in the nanochannels using electrochemical deposition. The tubes are then grown using a chemical vapor deposition system. In order to facilitate the measurement of the properties, the carbon nanotubes can be left in the aluminum template used for their growth. This method leads to a value for the mechanical properties of the aluminum template and the carbon nanotubes. In particular we are interested in the stiffness and hardness of the nanotubes; as such we intend to use nano-indentation and atomic force microscopy (AFM) to measure these properties. Detailed laboratory procedures can be found in the appendices of this report.

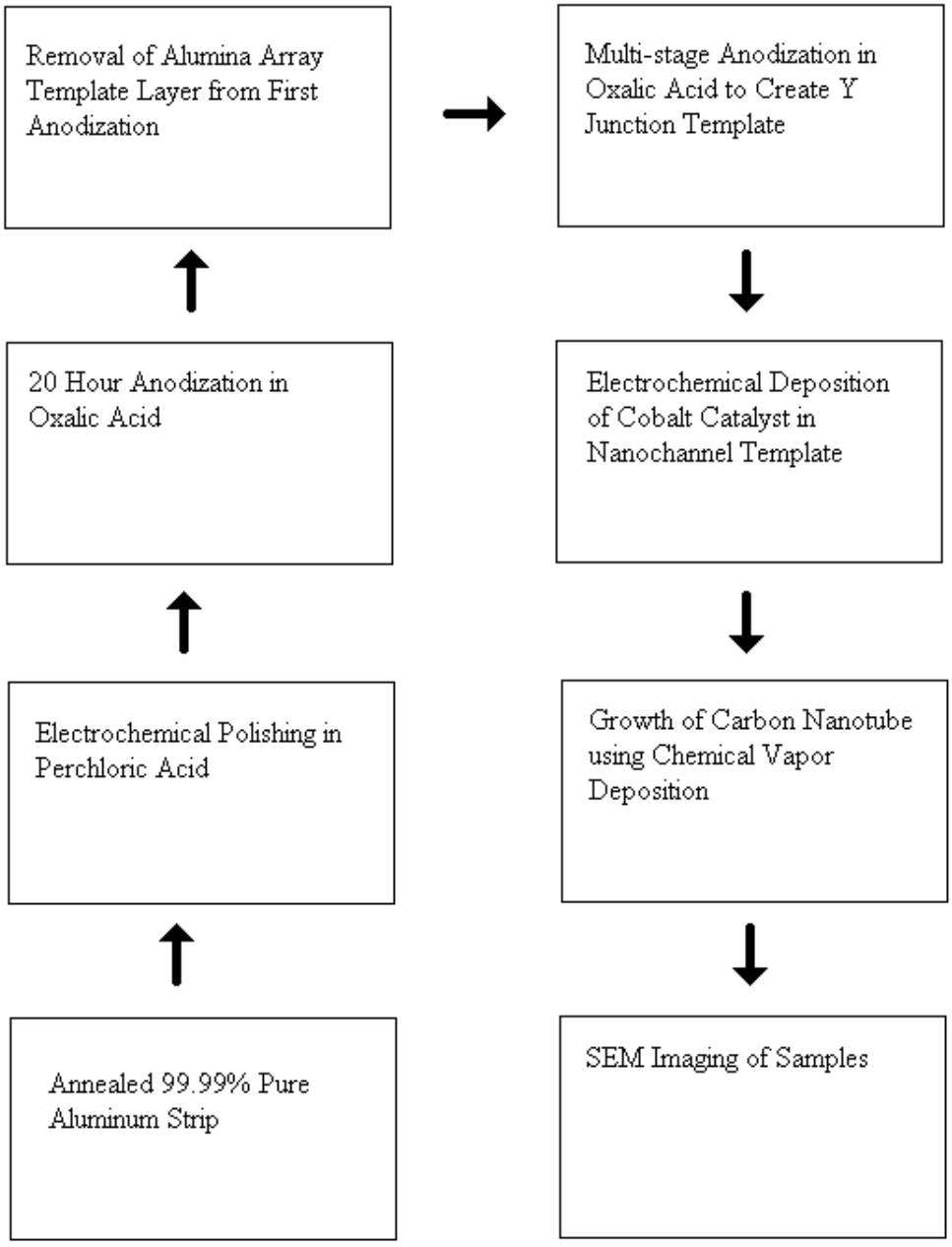

Figure 3-1: Diagram of Methodology Approach

3.1 Aluminum Preparation

3.1.1 Aluminum Annealing

The process begins with a strip of high purity (99.99%) aluminum that is 1mm thick by approximately 1cm wide and 6cm long. These strips of aluminum are placed in a tube that is sealed with glass wool at both ends to protect them from the environment of the furnace. This sealed tube is loaded into the furnace process tube, which is then sealed off to the atmosphere. Air is removed from the furnace gas system using a vacuum pump until the total flow through the system is 0 cubic centimeters per minute (cc/m or mL/min). The gas system is then closed, and high purity argon flows into the system until total flow through the system is again 0mL/min. The gas system is then opened to allow argon gas to flow through it. The flow of argon gas is configured to be between 50 and 100mL/min. The furnace is then turned on and heated up to 500°C, and the system is left under those conditions for 4 to 5 hours. The furnace is then shut off and the system is allowed to air cool to room temperature. After reaching room temperature the flow of argon gas is shut off. The process tube is then opened to the atmosphere, and the end seals are removed. Freshly annealed aluminum strips are taken out and ready for the next step in the treatment; template construction.

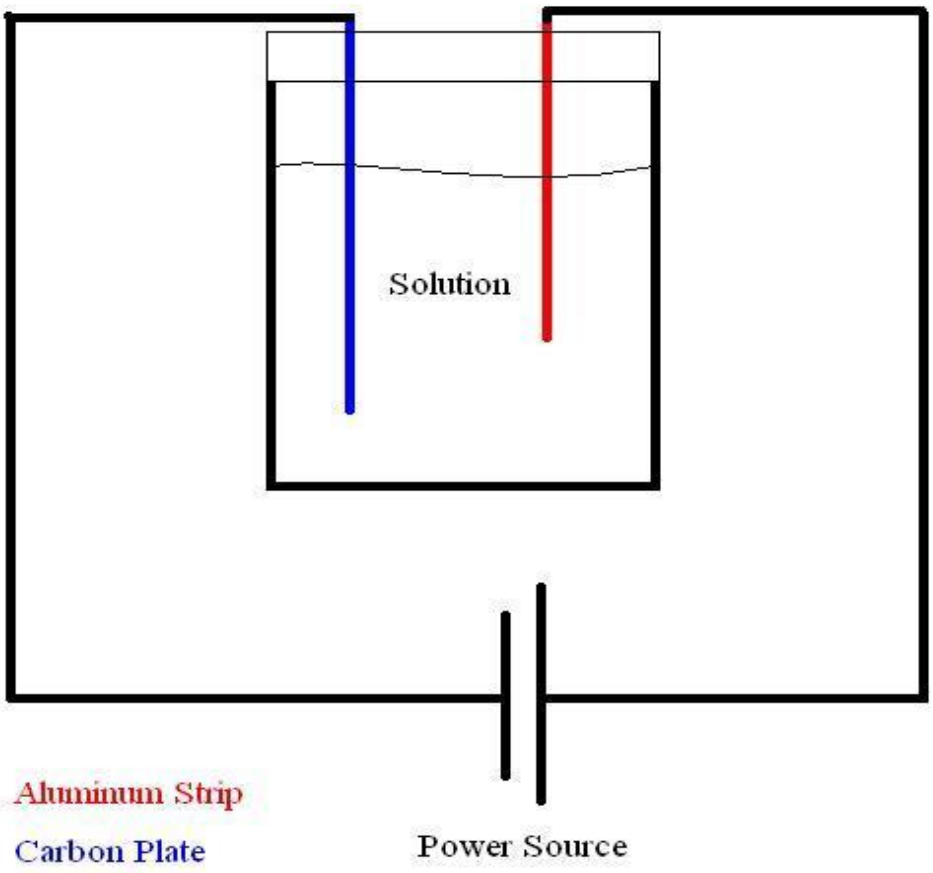

Figure 3-2: Simple Schematic of Electrochemical Polishing and Anodization Setup

3.1.2 Electrochemical Polishing

Annealed aluminum strip is electrochemically polished in a perchloric acid and dimethyl ether solution of volume ratio of 1 to 5 ($HClO_4 + 5C_2H_6O$) at 0° Celsius (C) for 4 minutes at 15 volts (V) direct current (DC). The polished strip of aluminum is then thoroughly cleaned with de-ionized water and dried off using lint free laboratory tissue.

3.2 Alumina Template Construction

3.2.1 Aluminum Insulation

The top of the back side of the aluminum strip is marked with a sample number in order to facilitate tracking of the sample. It is then covered with a light coat of clear nail polish, and a strip of Teflon tape is adhered to the strip using this thin coat of nail polish in order to insulate the rear side of the aluminum and prevent it from being anodized.

3.2.2 First Anodization

Once the back side of the strip has been covered in nail polish and Teflon tape, the sample is attached to an electric clip lead holder, which is then insulated using Teflon tape. The aluminum is then anodized in 0.3 molar (M) oxalic acid ($H_2C_2O_4$) at 10°C for a period of 16-24 hours at 40V DC. After this first anodization, the protective coating of Teflon tape and nail polish is then removed, and the substrate is cleaned in de-ionized water.

3.2.3 Removal of Alumina Template Layer

The freshly anodized strip of aluminum is then placed in a bath of 6 % H_3PO_4 + 1.8% Cr_2O_3 + de-ionized water at a temperature of 70°C for a period of about 4 hours. This step removes the Alumina layer created in the first anodization process, and leaves the substrate with a uniform distribution of indentations on the surface that will be widened and deepened during the second anodization process. The strips are then cleaned using de-ionized water.

3.2.4 Second Anodization

Similar to preparation for the first anodization, the back of the aluminum strip is covered with a layer of Teflon tape that is adhered to the sample using clear nail polish. Great care has to be taken to ensure that the edges of the strip are covered with Teflon tape as well to ensure that the back of the sample is properly insulated from the anodization process. The strip is then placed in 0.3 M oxalic acid at 10°C for a period of 30 minutes at 40V DC. The voltage is then gradually tuned downward to 28V DC, and the aluminum strips are left in the oxalic acid solution for another 40 minutes at 28V DC. The voltage is then slowly turned down while ensuring a positive current (greater than 1 milliamp) in small steps until a voltage of less than 10V DC is achieved. The samples are then removed from the oxalic acid solution, the Teflon tape and nail polish are removed, and the sample is thoroughly cleaned using de-ionized water.

3.2.5 Cobalt Deposition

The aluminum strips are again covered with a layer of Teflon tape using clear nail polish as an adhesive, with care to ensure that the edges of the aluminum strip are covered with Teflon tape. In order to be certain of this, a small portion of the Teflon tape is folded over the edge of the sample strips. The samples are then placed in a solution of 240 grams per liter (g/L) $CoSO_4*7H_2O$ + 40 g/L HBO_3 + 1 g/L $C_6H_8O_6$ at room temperature. The deposition takes place for 1 minute at 14V alternating current (AC) with a frequency of 100Hz. The deposited sample substrates are then cleaned with de-ionized water and the Teflon tape and nail polish are cleaned off the back of the aluminum strips.

3.3 CVD Growth

The anodized nanochannel templates are placed on a quartz boat and loaded into the furnace process tube. The ends of the process tube are sealed, the gas system closed off and all of the air inside the system is evacuated using a vacuum pump until no flow is recorded through the system. Then nitrogen gas is allowed to flow into the system until the flow meter indicates a 0mL/min flow rate. The system is then voided of nitrogen using the same procedure as was used for removing air. Carbon monoxide gas is introduced into the process tube until the flow meter indicates a 0mL/min flow rate. Then the system is opened, and a constant flow of 100mL/min of carbon monoxide gas is maintained through the system. The furnace is then turned on, heated up to 550°C and the system is at that temperature with carbon monoxide flow for one hour. After one hour, the temperature of the furnace is turned up to 560°C, the flow of carbon monoxide gas is turned off and acetylene gas is let to a flow at a rate of 100mL/min. The system is left for two hours. The acetylene gas is then turned off, and nitrogen gas is flowed through the system at 100mL/min while the furnace remains at 560°C. The system is then left under those conditions for 10 to 12 hours to anneal the carbon nanotubes. The furnace is turned off and allowed to cool under protective nitrogen gas flow. Finally the flow of nitrogen gas is stopped, and the freshly grown carbon nanotube samples are removed from the system.

3.4 Field Emission Scanning Electron Microscopy Results

For every stage of processing, two samples are taken. Those samples are examined under a scanning electron microscope to ensure that the desired intermediate properties

have been achieved. For example, after the removal of the alumina template layer prior to the second anodization, a highly ordered array of nanopores on the aluminum surface can be seen. By examining these samples at the high magnifications, we are able to confirm that our process produces the results we had expected. Using the SEM facilities at Harvard University, we were able to demonstrate that our process for preparing the nanochannel template was capable of creating Y junction nanochannels in the alumina substrate, and that we were successfully able to deposit nanoparticles of cobalt inside these nanochannels.

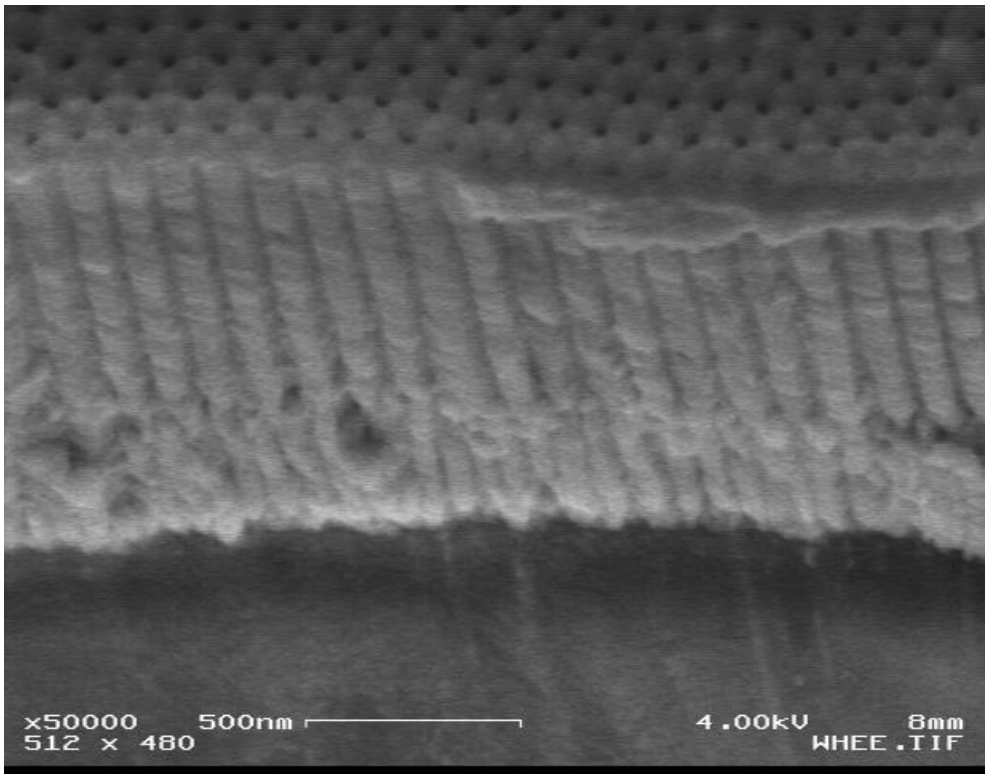

Figure 3-3: A SEM Image of Y Junction Nanochannels

4. Results and Discussion

One of the goals of this MQP project is to lay down a foundation of nanomaterials manufacturing for future groups of WPI students. When this project was started, there was very little equipment at WPI enabling nanomaterials fabrication and characterization. A major achievement of this project is the procurement and installation of necessary manufacturing equipment and the development and refinement of explicit nanomaterial manufacturing procedures (including the setups and procedures of anodization and chemical vapor deposition). In addition, we successfully used our setups to demonstrate the fabrication of Y-junction nanochannel templates and characterized the template by SEM. Other accomplishments include the building of a relationship with Harvard University to utilize expensive SEM equipment for imaging, and the accumulation of training materials for future nanomaterials projects.

4.1 Anodization Setup

We facilitated the installation and procurement of the equipment necessary to create the alumina templates with nanopore channels via a cobalt-based CVD process. The anodization setup includes stirring hotplates, a liquid chilling unit, a direct current power supply, a programmable alternating current power supply, jacketed beakers and the use of various chemicals specified in the procedure outlined in Chapter 3. We custom designed caps to hold the electrodes in the anodization and catalyst deposition processes, and had two caps machined out of ABS plastic. The accurate control of temperature was achieved through the use of a chiller in combination with the water jackets. We installed instrumentation to monitor and maintain so that the multiple processes involved can be

performed simultaneously. As a result, the equipment for the alumina template preparation was setup and organized inside the exhaust hood in our lab as shown in Figure 4-1 below.

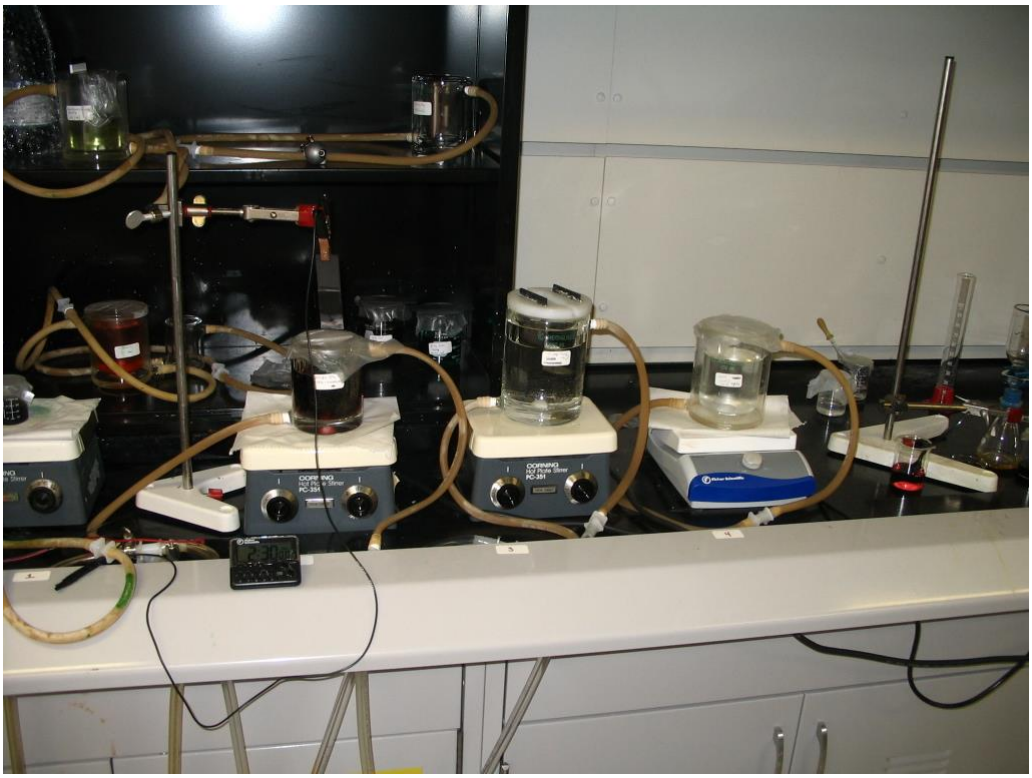

Figure 4-1: Picture of Anodization Setup

4.2 Chemical Vapor Deposition System

With the aide of project advisors, we designed the layout of the CVD system, detail designed and manufactured caps for the anodization equipment. It was installed by a certified plumbing company, as the system includes a hazardous gas monitor for safety purposes. Compressed gas cylinder training and compliance to OSHA standards for the installation of various cylinders were achieved. A schematic of the design of installed

CVD system is shown in Figure 4-2.

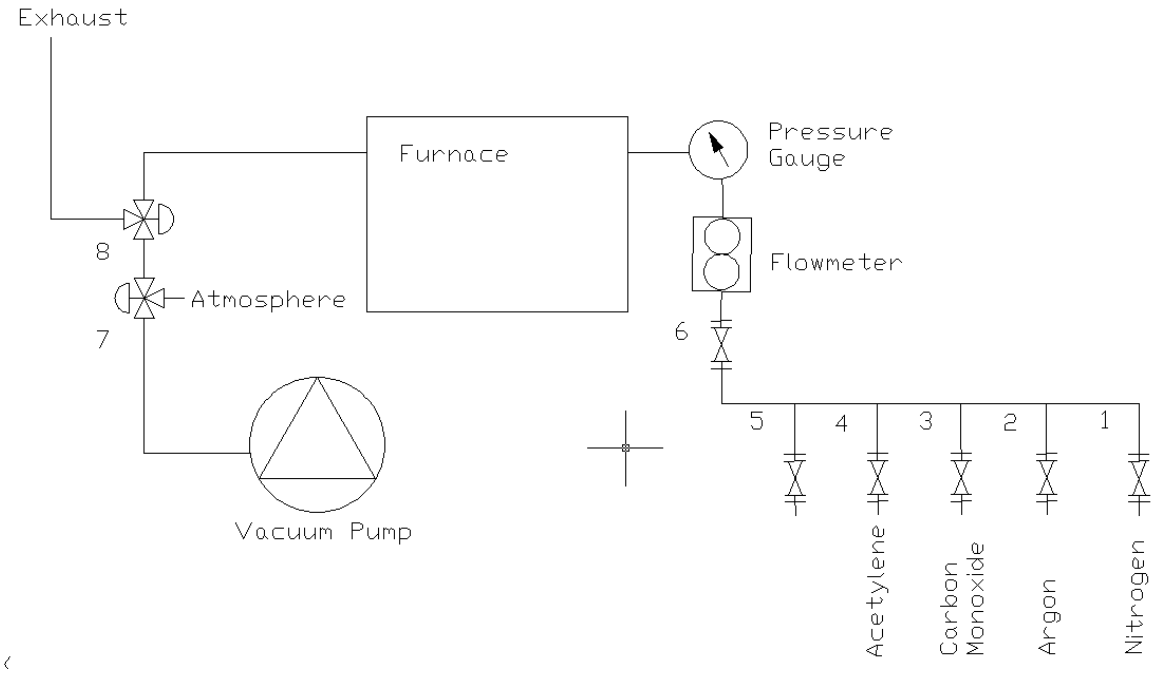

Figure 4-2: AutoCAD Drawing of CVD System Design

After the successful installation of the CVD system, and it was tested by annealing the aluminum strips used for anodization. Figure 4-3 shows the CVD system as it is installed in our Washburn 337 lab.

Figure 4-3: Picture of Installed CVD System

4.3 Written Procedures

With the preliminary research and layout of the CVD complete, it became necessary to develop explicit laboratory procedures for the aluminum annealing, alumina template construction and CVD growth of carbon nanotubes. We began by using a basic procedure for aluminum annealing and modified it to fit the specifics of our tube furnace and gases being used in our CVD system. We then took an existing procedure for creating a Y junction nanochannel in an alumina strip and adjusted it to meet our specific laboratory setup and equipment. Finally we took an established basic procedure for growing carbon nanotubes by pyrolisys of acetylene, and created a specific, sequential procedure to maintain appropriate sample temperature and gas flow using in the CVD system. These specific procedures can be found in the appendices at the end of this

report. A properly trained researcher can duplicate our work using the facilities at WPI by following the three laboratory procedures we have written. More information regarding our procedures is summarized in Table 4-1.

Procedure Name	Number of Steps	Appendix Number
Aluminum Annealing	31	7.3
Y Junction Alumina Template Preparation	25	7.1
CVD Growth of CNT	46	7.2

Table 4-1: Table of Procedures

4.4 SEM Results of Alumina Template

Following the procedures developed, we were able to fabricate an aluminum oxide template with Y-junction nanopores channels using our systems. Cobalt nanoparticles were deposited into those nanopores channels to serve as catalyst for the CNT growth. The as-fabricated nanopores channel templates were characterized by scanning electron microscopy. Figure 4-4 is an typical image of the top surface of our samples after the anodization, which demonstrates the ordered array of nanopores on the surface.

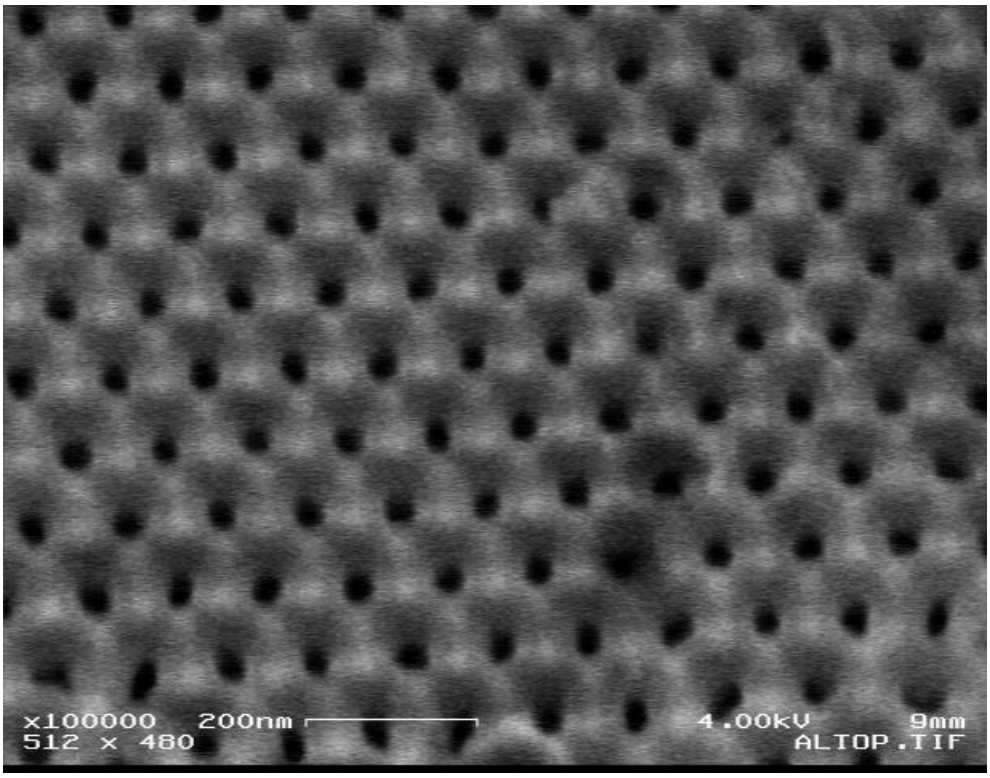

Figure 4-4: SEM Image of Nanopores After First Anodization

Figure 4-5 is an SEM image of one of our Y junction alumina templates prior to depositing cobalt in the nanochannels. We can see the ordered nanopores at the top surface and the branching of nanopores to form the Y-junction near the bottom. Figure 4-6 shows a sample after going through the cobalt depositing step, we believe the cobalt obscures the bottom of the nanochannels.

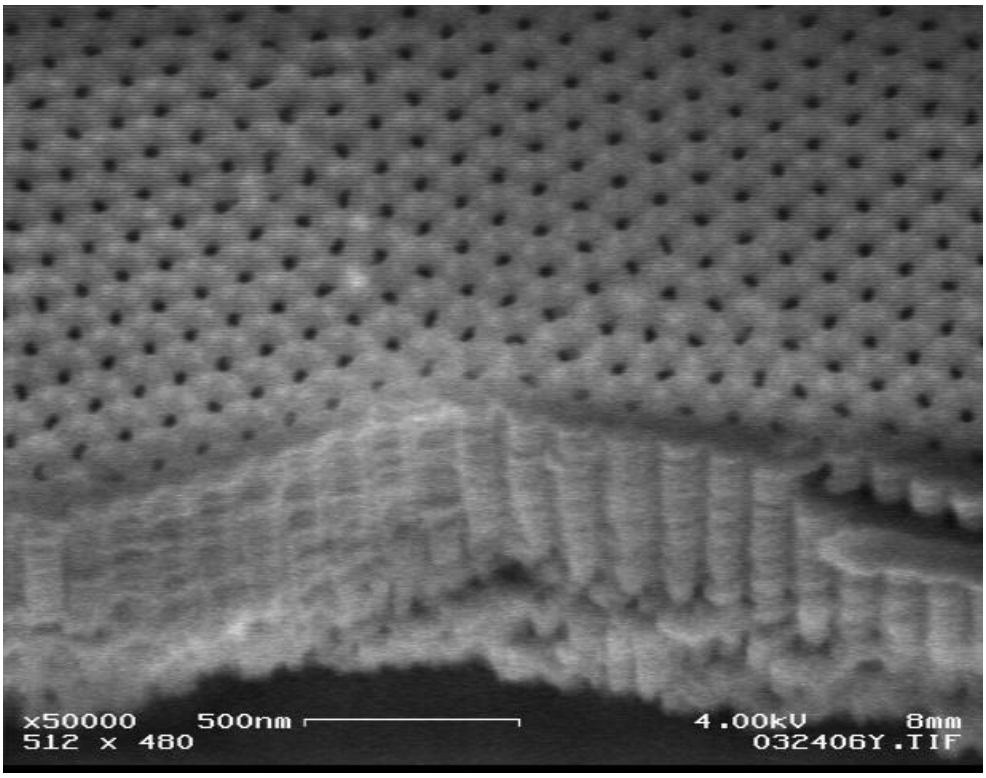

Figure 4-5: SEM Image of Y Junction Alumina Template

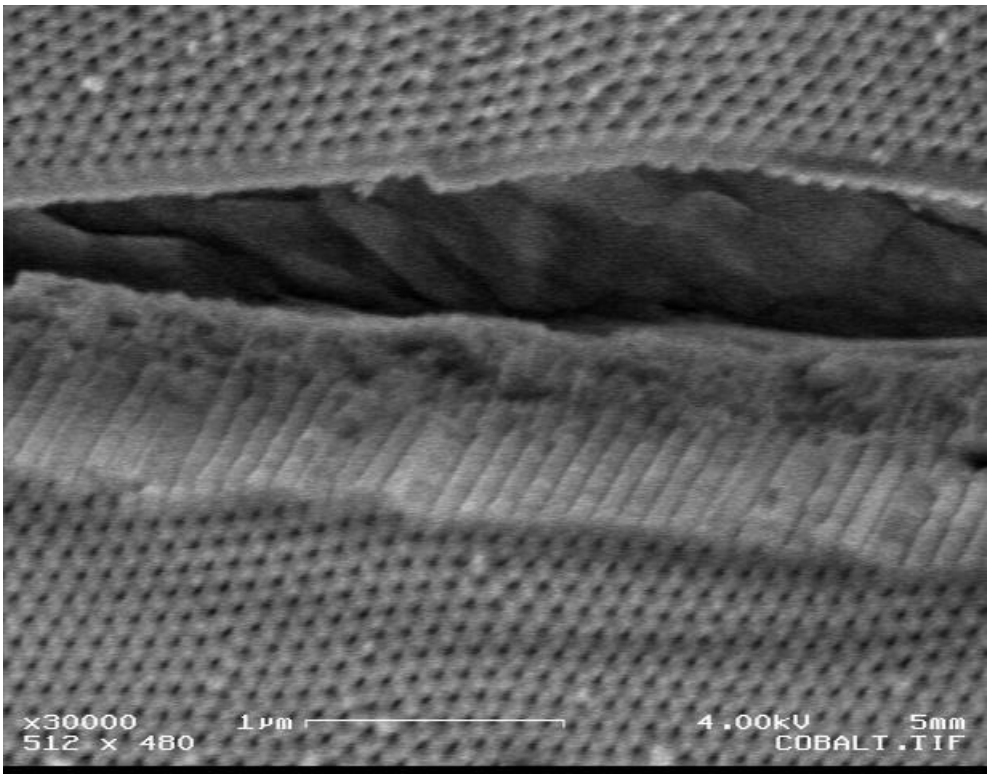

Figure 4-6: SEM Image of Cobalt Deposited Sample

5. Conclusions

Inspired by the unique structure of Gecko foot, we identified Y-junction carbon nanotubes as possible materials for mimicking this biological system. We successfully carried out the background study on Gecko foot, carbon nanotube, and characterization methods. We identified the template assisted fabrications as the suitable manufacturing method for Y-junction carbon nanotube growth and implemented the facilities to enable this manufacturing process. We also developed detailed manufacturing procedures and successfully produced Y-junction nanopores channel in aluminum oxide template through anodization. The results have been confirmed by SEM.

In the future, subsequent project groups will be able to use our research work as a foundation and grow Y junction carbon nanotubes using our procedures and characterize the mechanical properties using the methods identified by us. One critical issue facing the future groups will be anchoring of carbon nanotubes on carbon microfibers to mimic the hair structure of a gecko that inspired this project.

6. Works Cited

Bartlett, Richard D., and Patricia Bartlett. *Geckos: Everything about Selection, Care, Nutrition, Diseases, Breeding, and Behavior*. Hauppauge, NY: Barron's, 1995. Print.

Kendall, K. "Adhesion: Molecules and Mechanics." *Science* 263.5154 (1994): 1720-725. Print.

Bhushan, Bharat. *Springer Handbook of Nanotechnology / Bharat Bhushan (ed.).* Berlin ; New York: Springer-Verlag, 2004. Print.

Geim, A. K. Microfabricated adhesive mimicking gecko foot-hair. Nature materials 2.7 01 Jul 2003: 461-463. Nature Publishing Group. 09 Dec 2013.

Iijima, Sumio. "Helical Microtubules of Graphitic Carbon." *Nature* 354.6348 (1991): 56-58. Print.

Northen, Michael T., and Kimberly L. Turner. "A Batch Fabricated Biomimetic Dry Adhesive." *Nanotechnology* 16.8 (2005): 1159-166. Print.

Pierson, Hugh O. *Handbook of Chemical Vapor Deposition Principles, Technology, and Applications*. Norwich, NY: Noyes Publications, 1999. Print.

M. Sitti and R. S. Fearing, *Synthetic Gecko Foot-Hair Micro/Nano-Structures for Future Wall-Climbing Robots*, Proc. of IEEE International Conference on Robotics and Automation (ICRA ’03), 1, 1164- 1170, 14-19 Sept. 2003.

Srivastava, Deepak, Chenyu Wei, and Kyeongjae Cho. "Nanomechanics of Carbon Nanotubes and Composites." *Applied Mechanics Reviews* 56.2 (2003): 215-30. Print.

Sun, Wanxin, Pavel Neuzil, Tanu Suryadi Kustandi, Sharon Oh, and Victor D. Samper. "The Nature of the Gecko Lizard Adhesive Force." *Biophysical Journal* 89.2 (2005): L14-17. Print.

Yurdumakan, Betul, Nachiket R. Raravikar, Pulickel M. Ajayan, and Ali Dhinojwala. "Synthetic Gecko Foot-hairs from Multiwalled Carbon Nanotubes." *Chemical Communications* 30 (2005): 3799. Print.

Jiang, L., Y. Huang, H. Jiang, G. Ravichandran, H. Gao, K. Hwang, and B. Liu. "A Cohesive Law for Carbon Nanotube/polymer Interfaces Based on the Van Der Waals Force." *Journal of the Mechanics and Physics of Solids* 54.11 (2006): 2436-452. Print.

Nakajima, M., Zhan Yang, T. Fukuda, and F. Arai. "Measurement and Analysis of Interaction Forces between Carbon Nanotube Tip and Substrate." *2007 7th IEEE Conference on Nanotechnology: Hong Kong, China, 2-5 August 2007.* By Pou Liu. Piscataway, NJ: IEEE, 2007. 251-54. Print.

Autumn, K. "Mechanisms of Adhesion in Geckos." *Integrative and Comparative Biology* 42.6 (2002): 1081-090. Print.

"Timeline of Carbon Nanotubes." *Wikipedia*. Wikimedia Foundation, 26 Sept. 2013. Web. 09 Dec. 2013.

7. Appendices

7.1 Y Junction Alumina Template Procedure

1. Turn on chillers to bring $HClO_4 + 5C_2H_6O$ solution to 0° C and 0.3M $H_2C_2O_4$ acid solution to 10° C.

Electrochemical Polishing

2. Once $HClO_4 + 5C_2H_6O$ solution is at 0° C, turn on power supply and calibrate to 15VDC. Turn off power supply.
3. Mount sample on clip leads, and place samples in $HClO_4 + 5C_2H_6O$ solution, ensuring leads **do not** get into the solution, but sample substrate does.
4. Turn on power supply, connect and leave samples in solution for 4 minutes. Turn off power supply
5. Clean samples thoroughly of $HClO_4 + 5C_2H_6O$ solution using deionized water.

First Anodization

6. Paint the back side of sample substrate with nail polish and cover with Teflon tape, ensuring back and sides are completely covered.
7. Mount samples on clip leads, and cover clips and top of samples completely with Teflon tape in order to protect them from acid solution.
8. Turn on power supply and calibrate it for 40VDC, with some non-zero current (preferably 10-20mA). Turn off power supply.
9. Place sample substrates into 0.3M $H_2C_2O_4$ solution, turn on power supply and leave in solution for 16 hours or more.
10. Turn off power supply, remove samples, and clean thoroughly in deionized water.

Removal of Aluminum Oxide Layer

11. Remove Teflon tape and nail polish, and clean thoroughly with deionized water.
12. Place sample substrate in a solution of 6% H_3PO_4 + 1.8% Cr_2O_3 + deionized water at 70°C for at least 4 hours.
13. Clean thoroughly with deionized water.
14. Paint the back side of sample substrate with nail polish and cover with Teflon tape, ensuring back and sides are completely covered.

Second Anodization

15. Adjust chiller so 0.3M $H_2C_2O_4$ solution will be at 10° C.
16. Mount samples on clip leads, and cover clips and top of samples completely with Teflon tape in order to protect them from acid solution.
17. Turn on power supply and calibrate to 40VDC, turn off power supply.
18. Place sample substrates into 0.3M $H_2C_2O_4$ solution, turn on power supply and leave in solution for 30 minutes.
19. Slowly turn power supply to 28VDC. Leave samples in solution at this voltage for 40 minutes.
20. Slowly turn power supply down in small increments, ensuring a non-zero (1mA or larger) current to below 10VDC.
21. Turn off power supply, remove samples, and clean thoroughly in deionized water.

Preparation for Cobalt Deposition

22. Turn on power source to 14VAC, 0.1 kHz.
23. Place samples in 240 g/L $CoSO_4*7H_2O$ + 40 g/L HBO_3 + 1 g/L$C_6H_8O_6$ solution at room temperature under above voltage conditions for 1 minute.

24. Remove samples and rinse with deionized water.

25. Remove Teflon tape and nail polish, and clean thoroughly with deionized water.

7.2 CVD Growth of Carbon Nanotube Procedure

1. Place deposited sample substrate into quartz boat.
2. Ensure that all valves are in the off position.
3. Place quartz boat in the center of the process tube and seal both ends.
4. Turn on vacuum pump
5. Open valve 8 to direct flow to process tube.
6. Leave vacuum pump on until flow meter shows 0mL/min for more than 1 minute and pressure gauge reads high vacuum.
7. Close valve #8.
8. Turn off vacuum pump and open valve #7 to atmosphere.
9. Open valves #6 and valve #1.
10. Turn on nitrogen gas.
11. Allow nitrogen to flow into system until flow meter shows 0mL/min for more than one minute and pressure gauge reads close to driver pressure on regulator of nitrogen gas.
12. Close valve #6 and valve #1.
13. Turn off nitrogen gas.
14. Close valve #7.
15. Turn on vacuum pump
16. Open valve #8 to direct flow to process tube.
17. Leave vacuum pump on until flow meter shows 0mL/min for more than 1 minute and pressure gauge reads high vacuum.
18. Close valve #8.

19. Turn off vacuum pump and open valve #7 to atmosphere.
20. Open valves #6 and valve #3.
21. Turn on carbon monoxide gas.
22. Allow carbon monoxide to flow into system until flow meter shows 0mL/min for more than one minute and pressure gauge reads close to delivery pressure on regulator of carbon monoxide gas.
23. Open valve #8 to atmosphere.
24. Adjust carbon monoxide gas to maintain a constant flow of 60mL/min.
25. Turn on furnace to 550°C.
26. Leave at 550°C for 1 hour with carbon monoxide flow.
27. After 1 hour, increase temperature to 560°C.
28. Turn off carbon monoxide
29. Close valve #8 and valve #3.
30. Turn on acetylene gas.
31. Open valve #4 and valve #8.
32. Adjust flow of acetylene gas to 100mL/min flow.
33. Leave under acetylene gas flow for 2 hours at 560°C.
34. Turn off acetylene.
35. Close valve #8 and valve #4
36. Turn on nitrogen gas.
37. Open valve #1 and valve #8.
38. Adjust flow of nitrogen gas to 100mL/min flow.
39. Leave under nitrogen gas flow for 10 hours at 560°C.

40. Turn off furnace.

41. Allow furnace to cool, with nitrogen flow of 100mL/min.

42. Turn off nitrogen gas, close valve #1.

43. Close valve #6.

44. Ensure pressure gauge reads no pressure.

45. Open process tube ends.

46. Remove quartz boat.

7.3 Aluminum Annealing Procedure

1. Place aluminum strip in testing tube, seal end with glass wool.
2. Place testing tube in center of process tube, and seal both ends of process tube.
3. Turn on vacuum pump
4. Open valve #8 to direct flow to process tube.
5. Leave vacuum pump on until flow meter shows 0mL/min for more than 1 minute and pressure gauge reads high vacuum.
6. Close valve #8.
7. Turn off vacuum pump and open valve 7 to atmosphere.
8. Open valves #6 and valve #2.
9. Turn on argon gas.
10. Allow argon to flow into system until flow meter shows 0mL/min for more than one minute and pressure gauge reads close to driver pressure on regulator of argon gas.
11. Close valve #6 and valve #2.
12. Turn off argon gas.
13. Close valve #7.
14. Turn on vacuum pump
15. Open valve #8 to direct flow to process tube.
16. Leave vacuum pump on until flow meter shows 0mL/min for more than 1 minute and pressure gauge reads high vacuum.
17. Close valve #8.
18. Turn off vacuum pump and open valve #7 to atmosphere.

19. Open valves 6 and valve #2.
20. Turn on argon gas.
21. Allow argon to flow into system until flow meter shows 0mL/min for more than one minute and pressure gauge reads close to delivery pressure on regulator of argon gas.
22. Open valve #8 to atmosphere.
23. Adjust argon gas to maintain a constant flow of 50mL/min.
24. Turn on furnace to 500°C.
25. Leave at 500°C temperature for 4-5 hours with argon flow of 50mL/min.
26. Shut off furnace.
27. Allow system to cool with constant argon gas flow.
28. Close valve #2.
29. Shut off argon gas.
30. Close valve #6 and valve #8.
31. Open process tube and remove testing tube.

7.4 Anodization Cap Designs

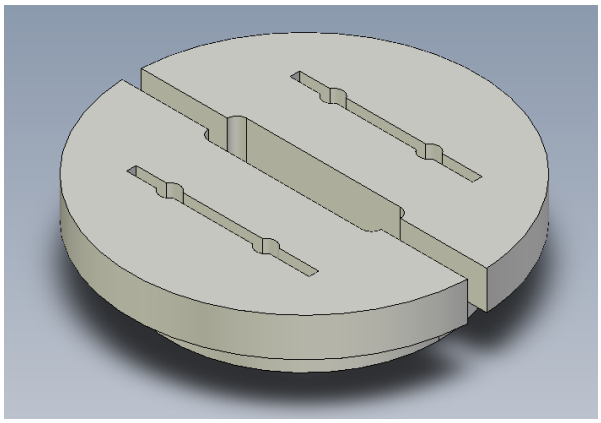

Figure 7-1 Side 1 Isometric View

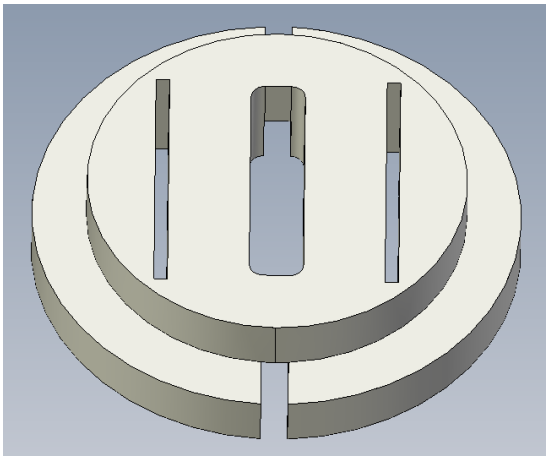

Figure 7-2 Side 1 Bottom View

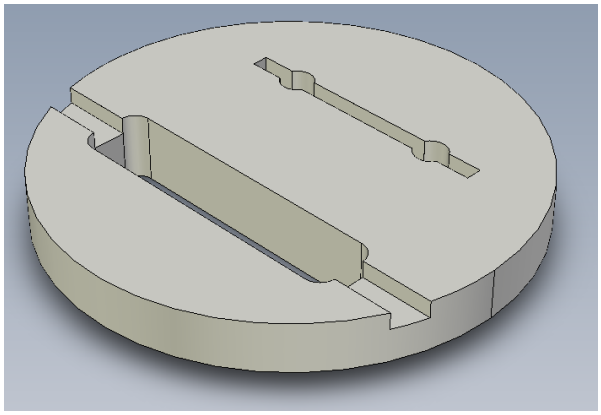

Figure 7-3 Side 2 Isometric View

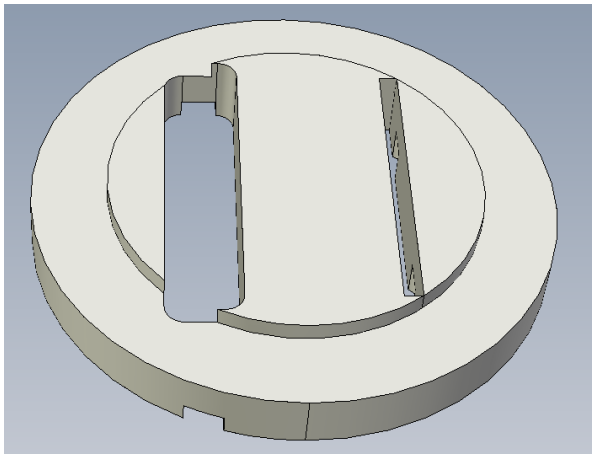

Figure 7-4 Side 2 Bottom View

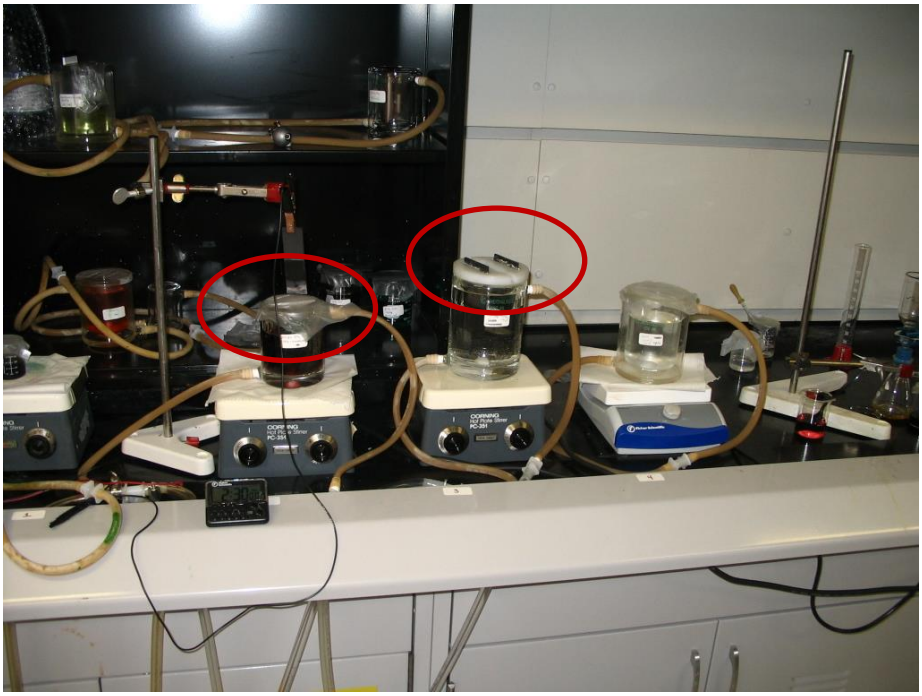

Figure 7-5 Caps Installed on Anodization Equipment